MULTI-ELEMENT METAL CONTINUOUS EMISSIONS MONITOR FOR COMPLIANCE MONITORING

TECHNOLOGY NEED

Draft EPA regulations for hazardous waste combustion include provisions for the use of continuous emission monitors (CEMs) for 6 toxic metals (arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb)) in stack gas emissions. In the draft rule, in order to create an incentive for the use of CEM technologies, release limits for these metals are somewhat higher for incinerators using CEMs rather than the standard monitoring techniques. The use of CEM technologies is being encouraged to secure the increased assurance of compliance afforded by continuous monitoring systems.

Currently, there are no commercial CEM technologies capable of meeting all of the detection limit requirements and data quality objectives of the proposed rule. The DOE has a number of incinerator sites that will be subject to the proposed regulation, when it comes into effect, and therefore has an interest in developing a CEM capable of meeting the EPA requirements. DOE incinerators that treat mixed waste have the additional need of monitoring for emissions of alpha-emitting materials, including isotopes of actinide elements (e.g., uranium (U) and plutonium (Pu)).

The conventional technology for monitoring elemental contaminants in stack gases is EPA Method 29. That Method is not a continuous monitoring technique at all, but is a protocol for sampling toxic metals from a gas stream for laboratory analysis. Method 29 is used during test burns to verify compliance for a specific range of combustion conditions and feed stream conditions. The EPA method is not continuous, involves long laboratory turnaround times, is fairly labor intensive (each sample requires careful collection and handling and a chain-of-custody paper trail), requires skilled laboratory staff for analyses, and provides little assurance to stakeholders that catastrophic releases do not occur. In addition, the costs for trial burns and the necessary analyses of the waste feed stream are high. Implementation of a CEM, such as the air, inductively coupled, plasma atomic emission spectrometer (ICPAES) with its high-resolution, will minimize and ultimately eliminate the need for extensive trial burns and feed stream characterization. CEMs will also give continuous, rapidly updated information on furnace operation, providing operator feedback and assuring regulatory compliance. Routine operation of the CEM may be automated, but a trained technician will be needed to perform periodic maintenance tasks.

The needs identified by Site Technology Coordination Groups (STCG) addressed by this project are as follows:

- OR WM-13: Metals Monitoring of Gaseous Emissions (PBS No. OR-38111)
- SR-1004: Demonstration of Continuous Emissions Monitors for Measurement of Hazardous Compound Concentrations in Incinerator Stack Gas (PBS No. SWR-SW01)
- ID-3.2.32: Develop Thermal Treatment Unit Off-Gas CEM Monitors (PBS No. ID-WM-101)

TECHNOLOGY DESCRIPTION

This project involves the development of a high-resolution, solid-state, compact spectrometer and detection system for monitoring spectral emission from an air ICPAES system. This fieldable detection system provides the resolution and sensitivity of a 1.0- to 1.5-m spectrometer in a package that is less than one-tenth the usual size and weight. The system consists of a 0.38-m echelle-grating spectrometer with an acousto-optic tunable filter (AOTF) performing grating-order selection. An array detector, either a linear photodiode array or a rectangular CCD array, detects the dispersed emission. The AOTF is a quartz crystal device that selects a narrow band (0.1-1.0 nm) of emitted light and rotates its polarization by 90 degrees. When placed between crossed polarizers, only the selected wavelength band is transmitted to the echelle grating. The AOTF wavelength is tuned by changing an applied radio frequency. The AOTF allows extremely rapid sequential or simultaneous selection of wavelengths with no moving parts. The wavelength-switching rate is limited to several milliseconds by the electronics and the speed of the acoustic wave in the quartz crystal.

Compared to more conventional echelle-grating spectrometers that utilize cross-dispersion gratings or prisms, this spectrometer provides advantages in reduced size, simplified optical components, reduced off-axis aberrations and light losses, minimized exposure of optical components to excessive UV source radiation, and smaller and less expensive detector requirements. Compared to tunable-grating spectrometers with comparable resolution, this detection system is smaller, lighter, provides more rapid wavelength tuning, and is more flexible than direct-reader spectrometers that require moving the detector components to change selected lines.

BENEFITS

This high-resolution, compact detection system enables the field operation of the air ICPAES CEM and other optical-emission based CEMs. It achieves this by reducing the size of the optical system while providing superior resolution for reduced spectral interferences and for the ability to measure isotopic composition of actinide materials in the sample stream. It allows deployment in areas where the size of conventional spectrometer instrumentation is a problem. It provides more rapid, user-programmable spectral switching than spectrometers of comparable resolution, and better resolution than spectrometers of comparable size. The advantages of this technology are that it makes the implementation of CEM technologies based on spectral emission more practical as alternatives to the conventional technology, and that it provides spectral resolution that makes on-line monitoring of isotopes of actinides practical. By enabling CEM technologies for toxic metals and actinides, this technology assures compliance with release limits, thereby minimizing risk to public health and maximizing public confidence.

CAPABILITIES/LIMITATIONS

Combined with the air ICPAES, this spectrometer/detection system can continuously monitor several metals in an off-gas stream. The system is completely solid-state and computer controlled with no moving parts. We have developed an extensive software control package that allows for easy spectral acquisition, calibration or standard additions, and continuous unattended monitoring. This software makes operation and maintenance by a well-trained technician feasible. The current sampling system for the air-ICP requires cycled sampling (15 seconds on/15 seconds off) due to the need to draw material from a reduced-pressure sample stream and inject it into the atmospheric pressure plasma of the ICP. This duty cycle and the sequential nature of the spectrometer may limit the number of elements that may be monitored during a single sample injection, depending on the integration time required for the desired detection limits. That limitation may be overcome by a number of measures.

First, the emission source (the ICP) may be configured to operate at a reduced pressure, continuously drawing sample into the plasma. Second, an AOTF may be incorporated into the spectrometer that may select more than one spectral window at a time. As long as these features do not overlap on the linear array detector, the system could be used as a simultaneous detector for a number of elements. For example, for the bench-scale prototype spectrometer assembled during FY 1998, the emission spectra for the selected emission lines of As, Be, Cd, Cr, Hg, Pb, ^{235}U and ^{238}U do not overlap on the detector and could be detected simultaneously using an AOTF capable of being excited at two or more frequencies.

COLLABORATION/TECHNOLOGY TRANSFER

The air ICPAES system has been developed and operated by the Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University. The air ICPAES is simply one of many possible emission sources that can effectively make use of the size, cost, resolution, and speed advantages of this detection system. We have begun discussions with developers at Massachusetts Institute of Technology who are working on a CEM based on a microwave induced plasma. We are also developing proposals with the Savannah River Site to apply this technology for monitoring the processing of spent nuclear fuel. The spectrometer technology is not patented, but has been offered for licensing by Iowa State University.

ACCOMPLISHMENTS

We participated in a demonstration of a previous generation spectrometer in partnership with a demonstration of the Diagnostic Instrumentation and Analysis Laboratory (DIAL) air-ICPAES at Mississippi State University in September 1997. We prepared a report detailing the results of that test and the performance of the detection system. Development of this next generation array-based echelle system in FY 1998 is in response to shortcomings of that previous system. The limitations included limited speed due to the scanning nature of a system using a single element detector, and limited resolution and range due to the optical coatings of the interferometer. The new generation system addresses all of those problems and will be demonstrated with the DIAL air ICPAES during FY 1998. The bench-scale prototype of this new system has been completed and shows significant improvement over the previous system in UV resolution (1 in 40,000) and wavelength coverage (200 - 425 nm). The improved wavelength range of the new detection system will permit the analysis of the isotopic composition of actinide materials as well as the monitoring of toxic metals.

TECHNICAL TASK (TTP) INFORMATION

TTP No./Title: CH17C233 - Development of a Multi-Element Metal Continuous Emission Monitor for Compliance

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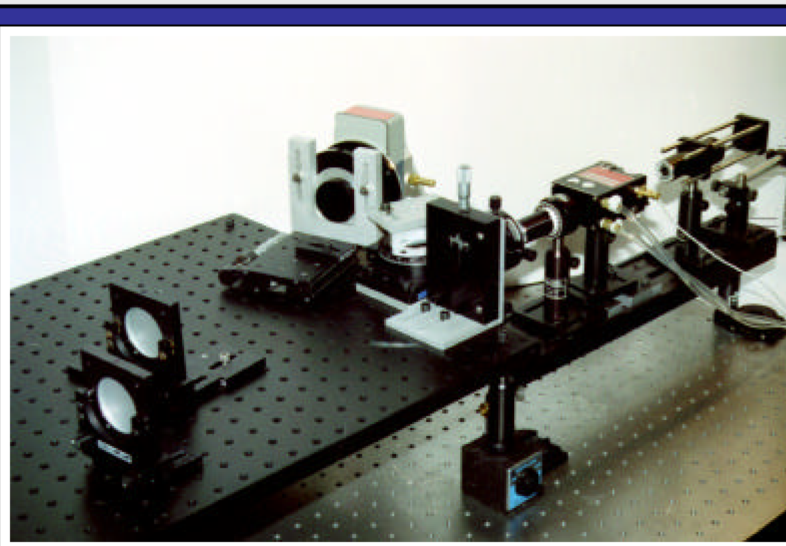

A high-resolution interferometric spectrometer is one of the instruments being tested to determine its capabilities for continuously monitoring toxic metals in DOE incinerators emissions to assure compliance with Draft EPA regulations.